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Self-consistency of Vuks equations for liquid-crystal refractive indices

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Vuks equations correlate the microscopic molecular polarizabilities to the macroscopic refractive indices of anisotropic crystalline materials. For anisotropic liquid crystals, the molecular polarizabilities are difficult to measure directly due to the short- and long-range interactions. We have converted Vuks equations into different forms. By measuring the refractive indices at different temperatures and wavelengths, the Vuks equations can be validated. Five liquid-crystal materials with refractive index ranging from ~1.46 to ~1.86 are used to validate the modified Vuks equations. The experimental results agree with the theory very well. Based on the Vuks equations, the molecular polarizabilities of 4-cyano-4-n-pentylbiphenyl are calculated. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1812356]

I. INTRODUCTION

Liquid crystals have been used extensively for displays,[1] laser beam steering,[2] and tunable photonic devices.[3] Most liquid-crystal (LC) devices utilize electric field, optical field, or thermal-induced refractive index change to modulate light.[4] The LC refractive indices are determined mainly by the molecular constituents, wavelength, and temperature.[5] Since LC is an anisotropic molecular system involving the short- and long-range molecular interactions, its refractive index is quite different from that of an isotropic liquid.

About four decades ago, Vuks proposed a semiempirical model[6] which is analogous to the classical Clausius-Mossotti equation for correlating the microscopic molecular polarizabilities to the macroscopic refractive indices of some crystalline materials. Based on the Vuks model, several phenomenological models have been developed to describe the wavelength and temperature dependencies of the LC refractive indices.[7–14] In the Vuks model, an isotropic local field is assumed. Vuks validated his model by using the experimental data of several anisotropic crystals such as naphthalene, diphenyl, anthracene, and phenanthrene.[6] Since the Vuks model has been used widely to describe the LC refractive indices, it is necessary to validate this model directly by using the experimental data of liquid-crystal materials.

To validate the Vuks equations for the LC molecular system is a challenging task because the LC molecular polarizabilities involve short-range and long-range interactions. In this article, we derive modified the Vuks equations and find that their validity can be easily examined by measuring the temperature- and wavelength-dependent refractive indices of liquid crystals. In Sec. II, we briefly discuss the derivation procedures. In Sec. III, the experimental method for measuring the refractive indices of liquid-crystal materials is briefly described. In Sec. IV, we describe the experimental results for validating Vuks equations using liquid-crystal materials. An excellent agreement between theory and experiment is obtained. Finally, we use Vuks equations to calculate the temperature-dependent polarizabilites of 4-cyano-4-n-pentylbiphenyl (5CB) at $\lambda = 589$ nm.

II. THEORY

The classical Clausius-Mossotti equation correlates the permittivity (ε) of an *isotropic* media with molecular polarizability (α) as follows:[15]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha. \tag{1}$$

In Eq. (1), N is the molecular packing density or number of molecules per unit volume. In the optical frequency regime, we substitute $\varepsilon = n^2$ and obtain the Lorentz-Lorenz equation:[15]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha. \tag{2}$$

For an anisotropic LC, there are two principal refractive indices, n_e and n_o, where n_e and n_o are refractive indices for the extraordinary ray and ordinary ray, respectively. In principle, each refractive index should be related to the corresponding molecular polarizabilities, α_e and α_o. An early approach replaces both n^2 in Eq. (2) by $n_{e,o}^2$and α by $\alpha_{e,o}$.[16] However, this model does not fit the experimental results well. Vuks made a bold assumption that the internal field in a crystal is the same in all directions,[6]

$$E_i = \frac{\langle n^2 \rangle + 2}{3} E, \tag{3}$$

where E_i is the internal field, the average field that acts on a molecule, and E is the macroscopic electric field. This assumption is later validated experimentally.[7] With this assumption, Vuks derived the following equation for *anisotropic* media:[6]

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$$\frac{n_{e,o}^2-1}{\langle n^2\rangle+2}=\frac{4\pi}{3}N\alpha_{e,o}. \tag{4}$$

Equation (4) is different from Eq. (2) in two aspects: (1) the n^2 term in the denominator of Eq. (2) is replaced by $\langle n^2\rangle = (n_e^2+2n_o^2)/3$, while the n^2 term in the numerator is replaced by $n_{e,o}^2$ and (2) the α is replaced by $\alpha_{e,o}$.

In Eq. (4), the macroscopic LC refractive indices n_e and n_o can be measured easily, however, the microscopic molecular polarizabilities α_e and α_o are difficult to determine directly. To validate Vuks equations, we rewrite Eq. (4) as follows:

$$\frac{n_e^2-1}{\langle n^2\rangle+2}=\frac{4\pi}{3}N\alpha_e, \tag{5a}$$

$$\frac{n_o^2-1}{\langle n^2\rangle+2}=\frac{4\pi}{3}N\alpha_o. \tag{5b}$$

Multiplying both sides of Eq. (5b) by 2 and then add the corresponding terms with Eq. (5a), we obtain the following equation:

$$\frac{(n_e^2+2n_o^2)-3}{\langle n^2\rangle+2}=\frac{4\pi}{3}N(\alpha_e+2\alpha_o). \tag{6}$$

Equation (6) can be rewritten as

$$\frac{\langle n^2\rangle-1}{\langle n^2\rangle+2}=\frac{4\pi}{3}N\langle\alpha\rangle, \tag{7}$$

where the average molecular polarizability is defined as $\langle\alpha\rangle=(\alpha_e+2\alpha_o)/3$. To evaluate Eq. (7) experimentally, we need to correlate $N\langle\alpha\rangle$ with another measurable macroscopic parameter, such as the average refractive index.

From Eq. (4), we can express n_e and n_o as follows:[13,14]

$$n_e=\left[1+\frac{4\pi N\alpha_e}{1-\frac{4}{3}\pi N\langle\alpha\rangle}\right]^{1/2}, \tag{8a}$$

$$n_o=\left[1+\frac{4\pi N\alpha_o}{1-\frac{4}{3}\pi N\langle\alpha\rangle}\right]^{1/2}. \tag{8b}$$

When $N\alpha_{e,o}$ is small, the term $4\pi N\alpha_{e,o}/(1-4/3\pi N\langle\alpha\rangle)$ is small and Eq. (8) can be expanded into power series,

$$n_{e,o}\approx 1+\frac{2\pi N\alpha_{e,o}}{1-\frac{4}{3}\pi N\langle\alpha\rangle}. \tag{9}$$

In the extreme case that $N\alpha_i\to 0$, the original Vuks equation [Eq. (4)] leads to $n_e\approx n_o\approx 1$. These results are consistent with Eq. (9). However, for most liquid crystals developed so far, their refractive indices are around 1.45–1.75. Therefore, the second term in the square root of Eq. (8) is larger than 1 but less than 2.1, the middle point is $\sim$1.5. Under such a circumstance, Eq. (8) cannot be expanded into power series directly. In order to make a series expansion, we rewrite Eqs. (8a) and (8b) as

$$n_e=\sqrt{2.5}\left[1+\frac{(x_e-1.5)}{2.5}\right]^{1/2}, \tag{10a}$$

$$n_o=\sqrt{2.5}\left[1+\frac{(x_o-1.5)}{2.5}\right]^{1/2}, \tag{10b}$$

$$x_{e,o}=\frac{4\pi N\alpha_{e,o}}{1-\frac{4}{3}\pi N\langle\alpha\rangle}. \tag{10c}$$

The absolute value of $(x_{e,o}-1.5)/2.5$ in Eqs. (10a) and (10b) is smaller than $\sim$0.2. By expanding Eqs. (10a) and (10b) into power series and keeping the first two terms, we obtain

$$n_e\approx\frac{7}{2\sqrt{10}}+\frac{(2\sqrt{10}/5)\pi N\alpha_e}{1-\frac{4}{3}\pi N\langle\alpha\rangle}, \tag{11a}$$

$$n_o\approx\frac{7}{2\sqrt{10}}+\frac{(2\sqrt{10}/5)\pi N\alpha_o}{1-\frac{4}{3}\pi N\langle\alpha\rangle}. \tag{11b}$$

During the series expansion, the second-order terms $(\sqrt{2.5}/8)[(x_{e,o}-1.5/2.5)]^2$ in Eqs. (11a) and (11b) are neglected because they contribute less than 0.57% to the entire refractive index values. The expressions (11a) and (11b) presented here are more accurate than those we derived earlier.[14]

In Eq. (11), the two refractive indices are still coupled through $\langle\alpha\rangle$. Our goal is to correlate the microscopic quantity $N\langle\alpha\rangle$ with a macroscopic measurable quantity, such as $\langle n\rangle$. To do so, we express the molecular polarizabilities α_e and α_o as[13]

$$\alpha_e=\langle\alpha\rangle+\frac{2S}{3}(\gamma_e-\gamma_o), \tag{12a}$$

$$\alpha_o=\langle\alpha\rangle-\frac{S}{3}(\gamma_e-\gamma_o). \tag{12b}$$

Substituting Eqs. (12a) and (12b) back to Eqs. (11a) and (11b), respectively, we can express n_e and n_o in terms of N, $\langle\alpha\rangle$, and $\alpha_e-\alpha_o$ [which is equal to $S(\gamma_e-\gamma_o)$] by power expansions,

$$n_e\approx\frac{7}{2\sqrt{10}}+\frac{(2\sqrt{10}/5)\pi N\langle\alpha\rangle}{1-\frac{4}{3}\pi N\langle\alpha\rangle}+\frac{(4\sqrt{10}/15)\pi NS(\gamma_e-\gamma_o)}{1-\frac{4}{3}\pi N\langle\alpha\rangle}, \tag{13a}$$

$$n_e\approx\frac{7}{2\sqrt{10}}+\frac{(2\sqrt{10}/5)\pi N\langle\alpha\rangle}{1-\frac{4}{3}\pi N\langle\alpha\rangle}-\frac{(2\sqrt{10}/15)\pi NS(\gamma_e-\gamma_o)}{1-\frac{4}{3}\pi N\langle\alpha\rangle}. \tag{13b}$$

Here, $\gamma_e-\gamma_o$ is the differential molecular polarizability in the crystalline state,[17,18] and S is the order parameter. In a temperature not too close to the clearing temperature (T_c), the order parameter can be approximated as follows:[19]

$$S=(1-T/T_c)^{\beta}. \tag{14}$$

In Eq. (14), the exponent β is a material constant. For many LC compounds, $\beta\sim 0.2$ is not too sensitive to the LC molecular structures.

Based on Eqs. (13a) and (13b), we can calculate the average refractive index, which is defined as $\langle n\rangle=(n_e+2n_o)/3$, and obtain the following equation:

$$\langle n\rangle \approx \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\langle\alpha\rangle}{1-\frac{4}{3}\pi N\langle\alpha\rangle}. \tag{15}$$

Equation (15) can be rearranged as follows:

$$1-\frac{3}{\sqrt{10}\langle n\rangle - 0.5} \approx \frac{4}{3}\pi N\langle\alpha\rangle. \tag{16}$$

Equation (16) correlates $N\langle\alpha\rangle$ to the average refractive index $\langle n\rangle$. This is an important step as the microscopic quantity $N\langle\alpha\rangle$ can be determined experimentally by measuring the LC refractive indices. In order to compare with Eq. (16), we rewrite Eq. (7) as

$$1-\frac{3}{\langle n^2\rangle + 2} = \frac{4}{3}\pi N\langle\alpha\rangle. \tag{17}$$

By comparing Eq. (16) with Eq. (17), we find

$$\langle n^2\rangle + 2 \approx \sqrt{10}\langle n\rangle - 0.5. \tag{18}$$

The significance of Eq. (18) is that the sophisticated microscopic Vuks equation can now be validated by two simple macroscopic parameters $\langle n^2\rangle$ and $\langle n\rangle$. These two parameters can be obtained by measuring the individual refractive indices (n_e and n_o) of the liquid crystal. In Sec. IV, we will use the experimental data of five LC materials with birefringence ranging from 0.08 to 0.35 to validate Eq. (18).

III. EXPERIMENT

We measured the refractive indices of UCF-35 (a high birefringence LC mixture), 5CB, 4-cyano-4-n-pentylecyclohexane-phenyl (5PCH), MLC-6241-000 (a commercial low birefringence LC mixture), and UCF-280 ($\Delta\varepsilon<0$) using a multiwavelength Abbe refractometer (Atago DR-M4) at $\lambda=450$, 486, 546, 589, 633, and 656 nm. The accuracy of the Abbe refractometer is up to the fourth decimal. For a given wavelength, we measured the refractive indices of these five LCs from 10 to 60 °C. The temperature of the Abbe refractometer is controlled by a circulating constant-temperature bath (Atago Model 60-C3). The LC molecules are aligned perpendicular to the main prism surface of the Abbe refractometer by coating a surfactant comprising of 0.294 wt % hexadecyletri-methyle-ammonium bromide in methanol solution. Both n_e and n_e are obtained through a polarizing eyepiece. From our measurements, the clearing points of UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280 are 368.3, 306.6, 325.9, 373.7, and 339.2 K, respectively.

IV. RESULTS AND DISCUSSIONS

We have measured the refractive indices of two LC compounds (5CB and 5PCH) and three eutectic mixtures [UCF-35, MLC-6241-000, and UCF-280 ($\Delta\varepsilon<0$)] at various wavelengths and temperatures. Their raw data are listed in Tables I–V, respectively.

Figure 1 depicts the temperature-dependent birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280 measured at $\lambda=589$ nm. The filled circles, squares, open circles, filled downward triangles, and open upward triangles are the measured birefringence of UCF-35, 5CB, 5PCH,

TABLE I. Measured refractive indices (n_e and n_o) of 5CB at $\lambda=546$, 589, and 633 nm at different temperatures.

	λ (nm)					
	546		589		633	
T (°C)	n_e	n_o	n_e	n_o	n_e	n_o
11.4	1.7566	1.5361	1.7448	1.5317	1.7361	1.5281
12.3	1.7549	1.5362	1.7431	1.5316	1.7342	1.5274
13.2	1.7531	1.5364	1.7414	1.5317	1.7328	1.5279
14.2	1.7511	1.5364	1.7396	1.5317	1.7309	1.5279
15.1	1.7493	1.5365	1.7378	1.5320	1.7289	1.5280
16.1	1.7475	1.5370	1.736	1.5323	1.7271	1.5283
17.0	1.7454	1.5373	1.734	1.5324	1.7253	1.5285
18.4	1.7421	1.5374	1.7309	1.5327	1.7222	1.5288
20.3	1.7378	1.5380	1.7264	1.5334	1.7181	1.5295
22.5	1.7316	1.5394	1.7205	1.5343	1.7123	1.5305
25.4	1.7232	1.5411	1.7124	1.5361	1.7038	1.5321
27.2	1.7165	1.5429	1.7059	1.5380	1.6977	1.5336
29.6	1.7056	1.5460	1.6954	1.5408	1.6876	1.5364
32.6	1.6819	1.5544	1.6724	1.5487	1.6654	1.5443
33.4	1.5940	1.5940	1.5872	1.5872	1.5820	1.5820
34.7	1.5938	1.5938	1.5868	1.5868	1.5815	1.5815
36.1	1.5927	1.5927	1.5859	1.5859	1.5809	1.5809
38.0	1.5919	1.5919	1.5849	1.5849	1.5795	1.5795
40.0	1.5907	1.5907	1.5840	1.5840	1.5785	1.5785
42.0	1.5899	1.5899	1.5831	1.5831	1.5776	1.5776
44.1	1.5887	1.5887	1.5820	1.5820	1.5770	1.5770
46.1	1.5876	1.5876	1.5810	1.5810	1.5758	1.5758
48.0	1.5868	1.5868	1.5801	1.5801	1.5748	1.5748
49.0	1.5865	1.5865	1.5797	1.5797	1.5745	1.5745
50.0	1.5859	1.5859	1.5793	1.5793	1.5739	1.5739
51.9	1.5850	1.5850	1.5783	1.5783	1.5729	1.5729
54.0	1.5838	1.5838	1.5771	1.5771	1.5723	1.5723

TABLE II. Measured refractive indices (n_e and n_o) of 5PCH at $\lambda=546$, 589, and 633 nm at different temperatures.

	λ (nm)					
	546		589		633	
T (°C)	n_e	n_o	n_e	n_o	n_e	n_o
24.9	1.6079	1.4907	1.6036	1.4878	1.6001	1.4854
30.1	1.6064	1.4904	1.6021	1.4873	1.5985	1.4849
34.1	1.6032	1.4893	1.5984	1.4866	1.5944	1.4842
39.2	1.5969	1.4890	1.5925	1.4861	1.5886	1.4835
44.2	1.5893	1.4888	1.5848	1.4861	1.5811	1.4833
49.3	1.5778	1.4902	1.5734	1.4875	1.5695	1.4844
50.4	1.5738	1.4911	1.5697	1.4883	1.5665	1.4856
51.9	1.5683	1.4933	1.5637	1.4901	1.5593	1.4869
52.9	1.5143	1.5143	1.5109	1.5109	1.5080	1.5080
54.2	1.5136	1.5136	1.5102	1.5102	1.5074	1.5074
55.2	1.5131	1.5131	1.5097	1.5097	1.5068	1.5068
56.0	1.5127	1.5127	1.5094	1.5094	1.5064	1.5064
57.0	1.5123	1.5123	1.5089	1.5089	1.5061	1.5061

TABLE III. Measured refractive indices (n_e and n_o) of UCF-35 at $\lambda = 589$, 633, and 656 nm at different temperatures. Blanks in the n_e column mean the refractive index is out of the measurement range of the Abbe refractometer.

	λ (nm)					
	589		633		656	
T (°C)	n_e	n_o	n_e	n_o	n_e	n_o
15		1.5375		1.5331		1.5315
20		1.5372		1.5329		1.5306
25		1.5370		1.5329		1.5311
30		1.5369		1.5328		1.5311
35		1.5373		1.5329		1.5316
40		1.5377		1.5331	1.857	1.5317
45		1.5383	1.8567	1.5336	1.8491	1.5319
47.4	1.8674	1.5385	1.8532	1.5337	1.8450	1.5321
50	1.8628	1.5389	1.8483	1.5343	1.8408	1.5324
52.4	1.8585	1.5391	1.8436	1.5345	1.8364	1.5326
55.1	1.8532	1.5398	1.8389	1.5349	1.8319	1.5329
57.4	1.8488	1.5401	1.8348	1.5355	1.8269	1.5331

MLC-6241-000, and UCF-280, respectively, at different temperatures. The temperature range for the experiment is from 10 to 55 °C. At room temperature and $\lambda = 589$ nm, the birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280 is 0.35, 0.2, 0.12, 0.086, and 0.085, respectively. The solid lines represent fittings using the Haller equation:[19]

$$\Delta n = (\Delta n)_o (1 - T/T_c)^{\beta}, \tag{19}$$

where $(\Delta n)_o$ is the LC birefringence at $T = 0$ K, β is a material constant, and T_c is the clearing temperature of the LC under studies. The clearing points for UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280 are 95.3, 33.4, 52.9, 100, and 66.2 °C, respectively. From these fittings, we find $[(\Delta n)_o, \beta] = [0.5727, 0.2719]$, [0.3505, 0.1889], [0.1706, 0.1512], [0.1221, 0.2209], and [0.1426, 0.2513], for UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280, respectively. Although UCF-280 has a larger $(\Delta n)_o$ than MLC-6241-000, its clearing temperature is much lower. As a result, its birefringence at room temperature is lower than that of MLC-6241-000 due to the order-parameter effect.

TABLE IV. Measured refractive indices (n_e and n_o) of MLC-6241-000 at $\lambda = 589$, 633, and 656 nm at different temperatures.

	λ (nm)					
	589		633		656	
T (°C)	n_e	n_o	n_e	n_o	n_e	n_o
11.7	1.5682	1.4796	1.5657	1.4779	1.5647	1.4771
13.5	1.5676	1.4794	1.5650	1.4772	1.5634	1.4765
16.6	1.5661	1.4782	1.5634	1.4762	1.5619	1.4755
21.2	1.5637	1.4768	1.5609	1.4744	1.5595	1.4738
25.2	1.5614	1.4753	1.5587	1.4739	1.5568	1.4729
29.9	1.5587	1.4742	1.5564	1.4724	1.5548	1.4714
34.5	1.5557	1.4727	1.5543	1.4712	1.5509	1.4699
39.9	1.5515	1.4706	1.5504	1.4697	1.5475	1.4683
44.6	1.5494	1.4695	1.5472	1.4682	1.5446	1.4671
49.4	1.5469	1.4678	1.5443	1.4662	1.5426	1.4655
53.7	1.5443	1.4673	1.5413	1.4651	1.5395	1.4640

TABLE V. Measured refractive indices (n_e and n_o) of UCF-280 at $\lambda = 589$, 633, and 656 nm at different temperatures.

	λ (nm)					
	589		633		656	
T (°C)	n_e	n_o	n_e	n_o	n_e	n_o
10.8	1.5783	1.4884	1.5751	1.4859	1.5739	1.4854
13.0	1.5771	1.4877	1.5735	1.4853	1.5725	1.4846
15.0	1.5756	1.4872	1.5720	1.4848	1.5709	1.4841
20.0	1.5722	1.4857	1.5685	1.4836	1.5677	1.4824
25.0	1.5682	1.4843	1.5649	1.4821	1.5638	1.4814
30.0	1.5644	1.4833	1.5613	1.4809	1.5598	1.4800
35.0	1.5600	1.4815	1.5569	1.4796	1.5558	1.4789
40.0	1.5554	1.4804	1.5522	1.4781	1.5511	1.4773
42.6	1.5529	1.4795	1.5497	1.4767	1.5484	1.4762
45.0	1.5499	1.4788	1.5471	1.4763	1.5450	1.4754
47.4	1.5477	1.4774	1.5445	1.4762	1.5430	1.4750
50.0	1.5445	1.4785	1.5411	1.4758	1.5396	1.4748
52.3	1.5413	1.4778	1.5381	1.4756	1.5370	1.4746
55.0	1.5370	1.4777	1.5335	1.4754	1.5325	1.4743

In Fig. 2, we plot the values of $(\langle n^2 \rangle + 2)$ and $(\sqrt{10}\langle n \rangle - 0.5)$ of 5CB and 5PCH in the same figure in order to validate Eq. (18) which is a close approximation of Vuks equation. The filled and open squares, circles, and upward triangles are the measured values of $\langle n^2 \rangle + 2$ and $\sqrt{10}\langle n \rangle - 0.5$ at $\lambda = 546$, 589, and 633 nm, respectively. From Fig. 2, we find that these data almost overlap each other. The difference is as small as ~0.2% for 5CB and ~0.1% for 5PCH. On the other hand, the average refractive index $\langle n \rangle$ decreases linearly as the temperature increases,[14]

$$\langle n \rangle = A - BT. \tag{20}$$

From Eq. (20), the right side of Eq. (18) can be written as

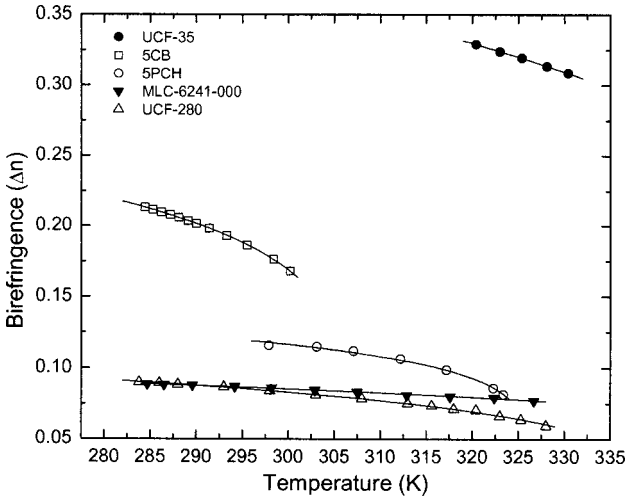

FIG. 1. Temperature-dependent birefringence (Δn) of UCF-35 (filled circles), 5CB (open squares), 5PCH (open circles), MLC-6241-000 (filled downward triangles), and UCF-280 (open upward triangles) at $\lambda = 589$ nm. The five solid lines are the fitting curves using $\Delta n = (\Delta n)_o (1 - T/T_c)^{\beta}$, where T_c is the clearing point.

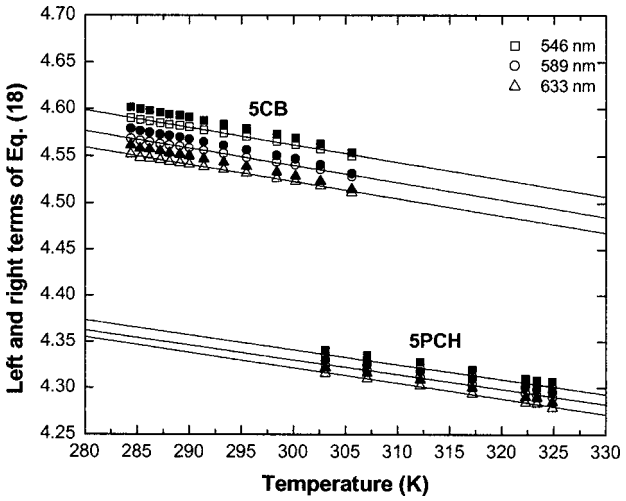

FIG. 2. Validation of Eq. (18) using the experimental data of 5CB and 5PCH. Filled squares, circles, and upward triangles are the calculated values of $\langle n^2\rangle+2$ at $\lambda=546$, 589, and 633 nm, respectively. Open squares, circles, and upward triangles are the corresponding values of $\sqrt{10}\langle n\rangle-0.5$. Solid lines are fitting results using Eq. (21). The fitting parameters are $[A,B]=[1.7751,\ 5.81\times10^{-4}]$, $[1.7674,\ 5.79\times10^{-4}]$, and $[1.7601,\ 5.75\times10^{-4}]$ for 5CB at $\lambda=546$, 589, and 633 nm, respectively. The corresponding [A, B] values for 5PCH are $[1.6837,\ 5.09\times10^{-4}]$, $[1.6795,\ 5.06\times10^{-4}]$, and $[1.6684,\ 4.82\times10^{-4}]$.

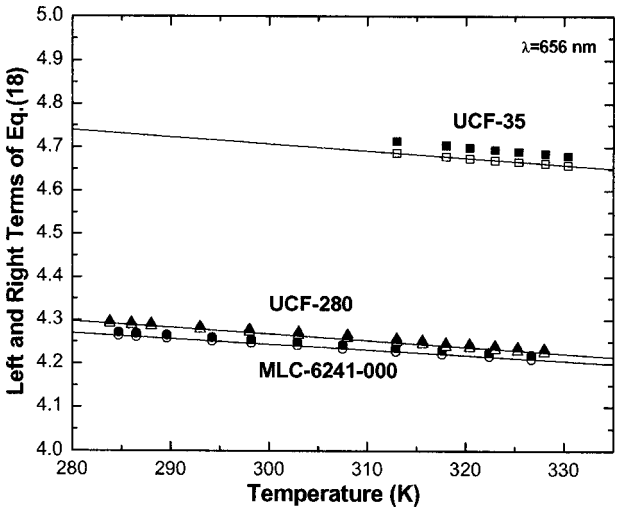

FIG. 3. Validation of Eq. (18) using the experimental data of UCF-35, UCF-280, and MLC-6241-000. Filled squares, circles, and upward triangles are the calculated values of $\langle n^2\rangle+2$ at $\lambda=656$ nm for UCF-35, MLC-6241-000, and UCF-280, respectively. Open squares, circles, and upward triangles are the calculated values of the corresponding values of $\sqrt{10}\langle n\rangle-0.5$. Solid lines are fitting results using Eq. (21). The fitting parameters are $[A,B]=[1.8003,\ 5.12\times10^{-4}]$, $[1.6216,\ 4.05\times10^{-4}]$, and $[1.6511,\ 4.79\times10^{-4}]$ for UCF-35, MLC-6241-000, and UCF-280, respectively.

$$\sqrt{10}\langle n\rangle - 0.5 = \sqrt{10}(A - BT) - 0.5. \tag{21}$$

The solid lines shown in Fig. 2 are the fitting results using Eq. (21). From Fig. 2, the agreement between experiment and fitting results is excellent for 5CB and 5PCH. The experimental data measured at different wavelengths and temperatures of 5CB and 5PCH all satisfy Eq. (18) very well. Therefore, Vuks equation is proven to be self-consistent for describing the refractive indices of LC compounds (5CB and 5PCH), although the isotropic local field is assumed.

Figure 3 shows a similar plot for UCF-35, MLC-6241-000, and UCF-280. The filled squares, circles, and upward triangles are the measured values for $\langle n^2\rangle+2$ at $\lambda=656$ nm for UCF-35, MLC-6241-000, and UCF-280, respectively. The open squares, circles, and upward triangles are the corresponding values for $\sqrt{10}\langle n\rangle-0.5$ at $\lambda=656$ nm. In Fig. 3, we plot the data at $\lambda=656$ nm because UCF-35 has more complete experimental data at this wavelength. The refractive indices of these three LC mixtures vary from $\sim$1.46 to $\sim$1.86, as listed in Tables I–V. Despite such variation, Eqs. (18) and (21) still hold very well.

In Fig. 3, all the experimental data of the left and right terms of Eq. (18) overlap quite well for UCF-35, MLC-6241-000, and UCF-280 although UCF-35 has 4$\times$ higher birefringence than the other two mixtures. The difference between the right- and left-hand terms of Eq. (18) is as small as $\sim$0.5% for UCF-35 and $\sim$0.1% for MLC-6241-000 and UCF-280. Solid lines are the fitting results using Eq. (21). The fitting results agree very well with the experimental data. Therefore, Vuks equation is proven to be self-consistent for both high and low birefringence LC mixtures.

As shown in Figs. 2 and 3, the $\langle n^2\rangle+2$ term is slightly larger than the $\sqrt{10}\langle n\rangle-0.5$ term. This is because we have omitted the higher order terms while deriving Eqs. (11a) and (11b) which, in turn, lead to Eqs. (16) and (18). The five LC materials we selected have refractive index spanning from $\sim$1.46 to $\sim$1.86. All the experimental data satisfy Eq. (18) quite well. It implies that the Vuks equation is valid for describing LC refractive indices independent of their molecular structures and electron conjugation length.

Since Vuks equation correlates the macroscopic refractive index to the microscopic molecular polarizability, if we know refractive index, then we can calculate the molecular polarizability or vice versa. For instance, if we plug the measured n_e and n_o data listed in Tables I–V back to Eq. (4), we can calculate the α_e and α_o values of the five LC compounds and mixtures at different temperatures and wavelengths.

In Eq. (4), there is still an unknown parameter N, the number of molecules per unit volume. However, N is equal to $\rho N_A/M$, where ρ is the LC density, M is the molecular weight, and N_A is the Avogadro's number. Rearranging Eq. (4), we find

$$\alpha_e = \frac{3M}{4\pi\rho N_A}\cdot\frac{n_e^2-1}{\langle n^2\rangle+2}, \tag{22a}$$

$$\alpha_o = \frac{3M}{4\pi\rho N_A}\cdot\frac{n_o^2-1}{\langle n^2\rangle+2}. \tag{22b}$$

Let us use 5CB as an example to calculate the molecular polarizabilities, α_e and α_o. For 5CB, the molecular weight is $M=249.3$ g/mol and the density $\rho(T)$ is taken from that measured by Zeller.[20] Using our measured refractive indices at $\lambda=589$ nm, we can calculate the α_e and α_o of 5CB from Eq. (22).

Figure 4 plots the temperature-dependent α_e, α_o, and $\langle\alpha\rangle$ of 5CB at $\lambda=589$ nm. The open and filled circles represent the calculated values for α_e and α_o, respectively. In the isotropic state, α_e and α_o are equal. The open triangles represent

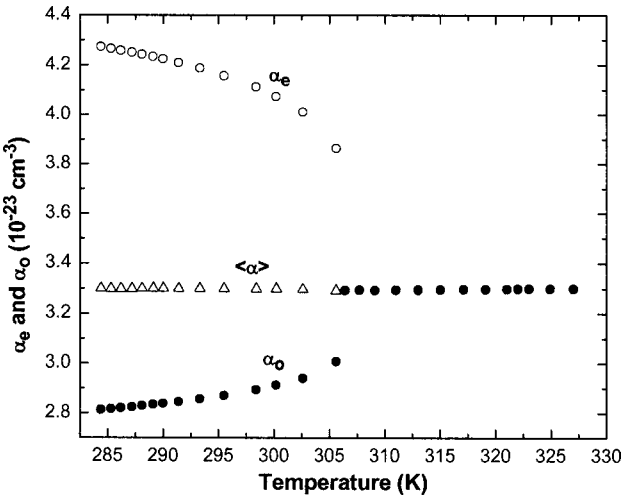

FIG. 4. Temperature-dependent molecular polarizabilites, α_e and α_o, of 5CB at $\lambda = 589$ nm. Open and filled circles are the results for α_e and α_o, respectively. Triangles represent the average polarizability $\langle\alpha\rangle$. In the isotropic phase, $\alpha_e = \alpha_o$.

the calculated average polarizability $\langle\alpha\rangle$ in the nematic phase. From Fig. 4, α_e decreases while α_o increases as the temperature increases. However, the average polarizability $\langle\alpha\rangle$ is quite insensitive to the temperature. The average polarizability for 5CB at $\lambda = 589$ nm is found to be $\langle\alpha\rangle \sim 3.3 \times 10^{-23}$ cm^{-3}, which agrees very well with the calculated value ($\langle\alpha\rangle \sim 3.25 \times 10^{-23}$ cm^{-3}) published by Sarkar *et al.*[21]

V. CONCLUSIONS

We have developed a simple method for validating Vuks equations. By decoupling n_e from n_o, we derived Vuks equations in a different form. We are able to correlate the molecular polarizabilities $\alpha_{e,o}$ to another macroscopic term $\langle n\rangle$. Through the derivation process, we find another relationship between $\langle n^2\rangle$ and $\langle n\rangle$, as described by Eq. (18). Using our experimental results, Vuks equation is validated despite that the isotropic local field is assumed. Based on Vuks equations, the molecular polarizabilities and average polarizability of 5CB at $\lambda = 589$ nm are obtained in the nematic and isotropic phases.

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[1] S. T. Wu and D. K. Yang, *Reflective Liquid Crystal Displays* (Wiley, New York, 2001).
[2] P. F. McManamon *et al.*, Proc. IEEE **84**, 268 (1996).
[3] H. Ren, Y. H. Fan, and S. T. Wu, Appl. Phys. Lett. **82**, 3168 (2003).
[4] N. V. Tabiryan, A. V. Sukhov, and B. Ya. Zel'dovich, Mol. Cryst. Liq. Cryst. **136**, 1 (1986).
[5] S. T. Wu, C. S. Wu, M. Warenghem, and M. Ismaili, Opt. Eng. **32**, 1775 (1993).
[6] M. F. Vuks, Opt. Spektrosk. **20**, 644 (1966).
[7] G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals* (Springer Verlag, Berlin, 1988), Chap. 10.
[8] S. T. Wu, Phys. Rev. A **33**, 1270 (1986).
[9] S. T. Wu, J. Appl. Phys. **69**, 2080 (1991).
[10] I. Abdulhalim, Mol. Cryst. Liq. Cryst. **197**, 103 (1991).
[11] I. C. Khoo and S. T. Wu, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore, 1993).
[12] E. M. Averyanov, J. Opt. Technol. **64**, 417 (1997).
[13] J. Li and S. T. Wu, J. Appl. Phys. **95**, 896 (2004).
[14] J. Li, S. Gauza, and S. T. Wu, J. Appl. Phys. **96**, 19 (2004).
[15] For example, see J. D. Jackson, *Classical Electrodynamics*, 2nd ed. (Wiley, New York, 1962).
[16] C. Bunn and R. Daubeny, Trans. Faraday Soc. **50**, 1173 (1954).
[17] A. D. Buckingham, in *Molecular Electro-optics*, edited by C. T. O'Konski (Marcel Dekker, New York, 1976), Chap. 2.
[18] L. M. Blinov, *Electro-optical and Magneto-optical Properties of Liquid Crystals* (Wiley, New York, 1983), Chap. 2.
[19] I. Haller, Prog. Solid State Chem. **10**, 103 (1975).
[20] H. R. Zeller, Phys. Rev. A **26**, 1785 (1982).
[21] P. Sarkar, P. Mandal, S. Paul, and R. Paul, Liq. Cryst. **30**, 507 (2003).